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SURFACE MODIFICATION OF POLYPROPYLENE BY PHOTOGRAFTING OF VINYL ACETATE MONOMERS

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Abstract: *The consumption of polymeric materials has increased in recent years. Among the wide variety of polymers, polyolefins are the most used at an industrial level. They have an optimal balance between processing and final properties, being used in low-technology sectors. There are some high technology sectors that require prior surface modification of polyolefins to improve the mechanical properties of adhesive joints. With this modification, the surface free energy is increased. The aim of this work was to modify the surface of polypropylene using the photopolymerization treatment. The surface free energy has been an increase of 175%, while the T-peel force has been increased 700%.*

Key words: *photopolymerization, vinyl acetate, adhesion, polypropylene.*

1. Introduction

Polypropylene is the most widely polyolefin used at an industrial level. It has an optimal balance between processability and final properties. It is used in areas of low and high technological content. Due to its apolar nature, it is chemically inert, which gives hydrophobic properties, i.e. low wettability and low surface activity. Therefore, it can’t be used in numerous industrial applications that require some surface activity, such as metal coating, painting and adhesive processes. So that, it is necessary to modify the polypropylene surface in order to increase its surface energy and, consequently, its surface activity.

There are different ways to modify and improve the surface wettability.

Firstly, there are treatments that use physical processes to achieve this. Among the wide variety of physical proceses, plasma treatments have incresed considerably [4]. The plasma is generated by exposing a gas between two electrodes between which, a high potential difference is generated. The projection of this plasma gas on the surface, promotes formation of free radicals, and this has a positive effect on surface activation. The projection of the gas also causes material removal from the surface (low molecular weight oxidized material - LMWOM) and this promotes changes in surface roughness. This phenomenon is known as microetching. There are three different types of plasma. One of the most useful plasmas is low-pressure glow discharge (LPGD) plasma,

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or “cold plasma”. It is possible to control a wide variety of variables (exposure time, electrode distance, plasma gas, gas flow rate, vacuum conditions…) but the main disadvantage is that this process must be carried out in a discontinuous way. Corona plasma is useful at an industrial level because it can be adapted to work online in a continuous way but it is characterized by some heterogeneity. Finally, the atmospheric plasma combines the advantages of the cold plasma and corona plasma, i.e. total control of process variables and continuous method of work. The use of plasma treatments leads to very good results, but from an economical point of view, they are very expensive and difficult to implement at an industrial scale.

The other way to modify a polymer surface, is by chemical processes. These are the most used because they require less investment for industrial implementation. The essence of treatment is to achieve surface modification by contact with chemical agents. The simplest method is to expose the surface to some specific reagents, which can cause surface abrasion and/or oxidation. In this method, the reagent consumption can be very high, which is not highly recommended from the environmental point of view. Thus arises the need of finding a chemical treatment in which the reagent consumption is very low. Among the treatments that meet this requirement, the photopolymerization [2] process shows interesing possibilities. It is characterized by a reduced consumption of reagents and high yields achieved in relatively short exposure times.

This process consists in grafting a base monomer onto the polypropylene surface. Usually, this base monomer must be highly polar, but in other situations for other purposes, it will be a monomer with other features. To perform this grafting process, it is necessary the presence for a photoinitiator to be present, which acts as a catalyst for the grafting reaction when exposed to ultraviolet radiation. The photoinitiator can be applied individually or together with the base monomer. Therefore, according to the way of implementation of the photoinitiator, there are two types of photopolymerization. The first type is known as photopolymerization or “one step”. Both the monomer and the photoinitiator are dissolved within the same solvent and they are applied onto the polymer surface for subsequent exposure to UV radiation. After exposure to UV light, the photoinitiator decomposes and forms free radicals. These act as points of attachment of base monomer chains. The second type is called sequential photopolymerization or “two step” and it is carried out in two steps. Initially, only the photoinitiator is applied on the polymer surface, and it is irradiated with UV light. This will create the interlock points for the next step, in which the base monomer is applied in a particular solvent and re-irradiated with UV light. Base monomer chains are attached to the surface through the interlock points created in the first step.

This work focuses on photo-polymerization in a single step. This is a very versatile process or treatment. It supports a wide variety of monomers and substrates. In most cases, the polymer is used in film format. This format ensures homogeneity of results, thus achieving high performance for relative short exposure times. Different base monomers can be used (depending on the ultimate use of the treated polymer). In most cases, the base monomers used are highly polar, such as acrylic acid (AA) [1], vinyl acetate (VAc), methyl methacrylate (MMA) [3]. These monomers improve the surface wettability and consequently, adhesive properties. In other cases, base monomers with hydrophobic properties allow to create self-cleaning surfaces. The solvent must be selected to ensure good solubility of both monomer and photoinitiator. The most commonly used solvents are: acetone, methanol, chloroform, cyclohexane. Another variable that must be taken into account is the exposure time to UV radiation. This will vary depending on the radiation power and distance of application of the source of UV light. The use of low powers requires the use of shorter distance. The electrical power of the UV lamp used was 1000W. The application distance was 20 cm. And the exposure times ranged from 30 to 240 with intervals of 30 seconds.

The aim of this work was to evaluate the usefulness of one step photografting for surface activation of polymer surface. Polypropylene was used as a polymer substrate. The base monomer was vinyl acetate (VAc) characterized by high polarity. The photoinitiator used was benzophenone (BP), and the solvent was acetone. To evaluate the effects of the VAc photografting process, contact angles for different liquids were measured and the surface free energy was calculated. Thus, the change in surface wettability was checked. The chemical changes produced on the polypropylene surface after the treatment were studied by FTIR-ATR analysis. Finally, adhesive PP-PP joints were characterized by *T*-peel tests.

2. Experimental

2.1. Materials

The polypropylene used was the ISPLEN PB 180 G2M and it was supplied by Repsol YPF. It was injected and cut into squares of 1x1 cm^2. The base monomer used was a vinyl acetate supplied by Acros Organics. The photoinitiator used was benzophenone, and it was supplied by Scharlau Chemie. Regarding the solvent, acetone reagent grade was used. Measuring of contact angles was carried out with four different test liquids: water, diiodomethane, formamide and glycerol. For the mechanical characterization of adhesive joints it was used a reactive polyurethane adhesive to form PP-PP adhesion joints. It was supplied by Kefren and responding to the commercial name 801 Grey Polyurethane.

2.2. Characterization of wetting changes

Changes in the surface of polypropylene after treatment were tested by measuring the contact angle with four test liquids. The equipment used was a KRÜSS Easydrop STANDARD goniometer, model FM140. The equipment has a video camera that can observe the image of the drop on the substrate. It also has computer software that performs the analysis and calculates the corresponding angle. Then the surface free energy was calculated using the Owens-Wend method. This method takes into account the polar and dispersive components. The Owens-Wendt expression corresponds to an expression of the general form $y = a + bx$, and the formula is:

$$\gamma_1 \frac{1+\cos(\theta)}{2(\gamma_l^d)^{1/2}} = (\gamma_s^p)^{1/2}\left[\frac{(\gamma_l^p)^{1/2}}{(\gamma_l^d)^{1/2}}\right] + (\gamma_s^d)^{1/2}, \quad (1)$$

where θ is the contact angle, γ_l is the total surface free energy of the liquid and γ_s represents the surface free energy of the solid. The terms with subscripts "*d*" and "*p*" refer to the "dispersive" and "polar" component of the surface free energy. We can see in an easy way that the previous equation can be expressed as a linear expression ($y = a + bx$). So that, we can represent $[(\gamma_l^p)^{1/2}]/[(\gamma_l^d)^{1/2}]$ versus a $[\gamma_l (1 + \cos\theta)]/[(\gamma_l^d)^{1/2}]$. Then, the slope of the line will be $(\gamma_s^p)^{1/2}$ and the y-axis intercept will be $(\gamma_s^d)^{1/2}$. The total solid surface free energy (γ_s) will be calculated as the sum of the polar (γ_s^p) and dispersive (γ_s^d) component.

2.3. Characterization of chemical changes

To characterize the chemical changes produced as a result of the photografting process, Fourier transform infrared spectroscopy (FTIR) with attenuated total reflectance (ATR) accessory was used. The equipment used was a Perkin Elmer Spectrum BX with an ATR accessory, model Pike Miracle Technologies. Scans were made at wavenumber ranging from the 2000 and 600 cm^{-1}.

2.4. Characterization of adhesion joints

T-peel tests were performed to verify the improvement of adhesion properties. These tests were carried on PP-PP adhesion joints. The equipment used was a universal tensile machine ELIB 30, Ibertest.

3. Results and Discussion

3.1. Characterization of wetting changes

The contact angle obtained by placing a drop on the polypropylene surface has been measured. This was done for four different reference liquids. These measurements were performed on samples with different exposure times to UV light. Figure 1 shows graphically the evolution of the contact angle values as a function of exposure time for two reference liquids, formamide and glycerol.

It can be noted that for both formamide and glycerol, the minimum value of contact angle is obtained for an exposure time of 120 seconds. There is a decrease in the value of contact angle from 71.38° to 32° and 74.67° to 46.9° for the formamide and glycerol respectively. This represents a decrease of 55% and 37%. This decrease in contact angle is a direct consequence of the grafting of chains of a highly polar monomer.

Once the contact angles for the four test liquids were obtained, the surface free energy was calculated according to the Owens-Wendt model described previously. Figure 2 shows a plot of the evolution of the values of surface free energy obtained according to expression (1). This figure also shows the contributions to the total value of both components, the polar and dispersive. It can be observed that the surface free energy increases with the exposure time to UV radiation. This is mainly due to the contribution of the polar component, since the dispersive component remains almost constant.

As expected, the highest value of surface free energy corresponds to an exposure time of 120 seconds. This value changes from

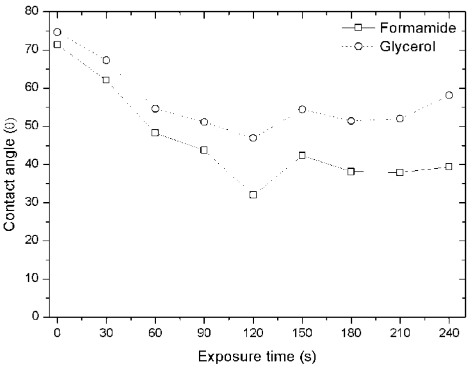

Fig. 1. *Evolution of contact angle versus exposure time for different test liquids*

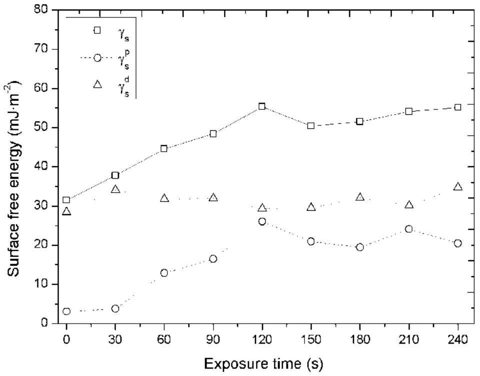

Fig. 2. *Evolution of surface free energy and its polar and dispersive component in terms of the exposure time to UV radiation*

31.48 mJ·m^{-2} for untreated polypropylene up to 55.32 mJ·m^{-2} for 120 seconds, thus representing a percentage increase of 175%. The evolution of the surface free energy is inversely proportional to the contact angle. Therefore it is shown that the photografting treatment produces important changes in the polypropylene surface.

3.2. Characterization of chemical changes

There are several techniques to check the chemical changes produced on the polypropylene surface after the treatment. The most used technique is Fourier transformed infrared spectrocospy (FTIR). In our case, an attenuated total reflectance (ATR) accessory has been used, since the samples are not transparent and we wanted to detect changes in a small layer. Using this technique, different scans were made and characteristic bands were analyzed. Some bands are characteristic of the polypropylene while others are the result of the photografting process of vinyl acetate by UV radiation. Figure 3 shows the FTIR spectra for three different samples. The first spectrum corresponds to untreated polypropylene. The other two spectra correspond to samples with an exposure time of 60 and 120 seconds to the photografting process.

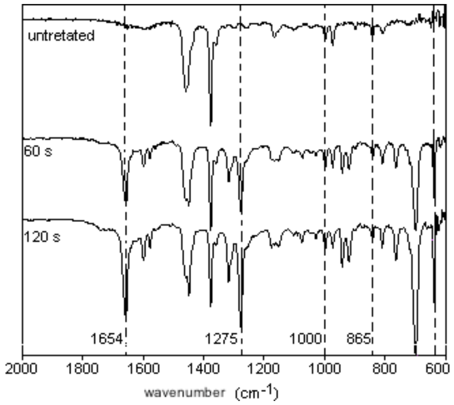

Fig. 3. *FTIR spectra of untreated and vinyl acetate photografted polypropylene with different exposure times*

Bands obtained at wavenumbers of 1654 and 1275 cm^{-1}, correspond to the decomposition of benzophenone. The bands of 1000 and 865 cm^{-1}, are due to the grafting of vinyl acetate chains.

In all cases, it can be observed that the bands increase in intensity with increasing exposure time. This is mainly due to increased rate of graft chains of vinyl acetate monomer.

3.3. Characterization of adhesion joints

Finally, we performed a *T*-peel test to check the effectiveness of photografting process. The adhesion properties of polypropylene improved dramatically. Figure 4 shows graphically the value of the *T*-peel force as a function of exposure time.

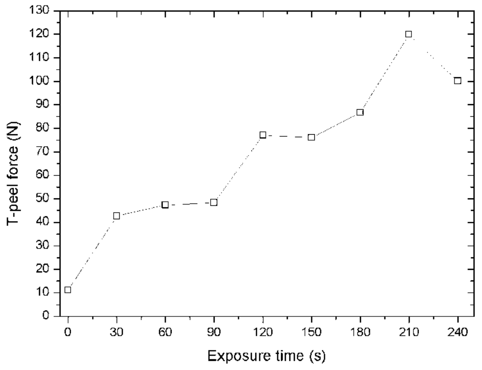

Fig. 4. *T-peel force*

It is noted that the value of the *T*-peel force increases with exposure time. It changes from a value of 11.07 N for an untreated sample to a value of 77 N for 120 seconds of exposure time. This represents an increase of almost 700%. Therefore it is shown that the photografting treatment produces a marked improvement in the mechanical properties of PP-PP adhesion joints. The maximum value of the *T*-peel force is obtained for an exposure time of 210 seconds. This value has not been taken into account because for these exposure times, the sample may have undergone degradation.

4. Conclusions

It has been demonstrated that the surface properties of polypropylene have been improved through a UV photografting process, using vinyl acetate as a base monomer and benzophenone as photoinitiator.

The surface free energy for a sample treated with 120 seconds of exposure time represents an increase of 175% over the value of an untreated sample. Therefore, it is demonstrated the loss of hydrophobicity of the polypropylene after treatment.

By FTIR-ATR it has been shown that vinyl acetate chains have been grafted on the surface of polypropylene. The rate of grafting increases with exposure time.

Finally, it has been demonstrated that the adhesion properties have improved significantly. These have been increased by almost 700%.

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